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Measuring Inorganic and Alkyl Lead Emissions from Stationary Sources

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Described are the results from studies done to provide test methods for state and local air pollution control agencies to measure accurately the lead emissions from stationary source stacks as required in the National Ambient Air Quality Standard for Lead. Separate test methods were developed for measuring inorganic lead and alkyl lead compounds. Inorganic lead is collected in a standard particulate sampling train, digested with 50% (V/V) nitric acid and 3% hydrogen peroxide and analyzed by atomic absorption spectrometry. Alkyl lead compounds are collected in iodine monochloride and analyzed by atomic absorption spectrometry without prior solvent extraction. Standard solutions of inorganic lead in dilute nitric acid are used to calibrate the spectrophotometer in both methods. The inorganic lead test method was evaluated using baghouse dust samples from a primary copper and a primary lead smelter and stack samples from a lead recovery furnace, a primary battery manufacturing plant, a gray iron foundry and a secondary lead smelter. The alkyl lead method was evaluated using alkyl lead motor mix fluids and samples from an alkyl lead manufacturing plant vent stack.

The U.S. Environmental Protection Agency (EPA) has promulgated a National Ambient Air Quality Standard (NAAQS) for lead[1] that requires each state to construct an emissions inventory for all stationary sources which may emit 5 tons or more of lead per year. If existing data are inadequate to construct this inventory, then the state may need to conduct ambient air and stack testing to estimate the emissions from some sources. Stack testing may also be required to identify the specific source(s) responsible for an air pollution episode.

To assist the states in those special cases where stack testing is required, EPA developed and evaluated test methods to measure the Pb emissions from the types of stationary sources likely to be included in the emissions inventory. Two test methods were developed, one for inorganic Pb and the other for alkyl lead compounds. Described below are the laboratory and field studies done in developing and standardizing these two test methods. The test methods themselves are described in detail in a background document which accompanied the standard.[2]

Development of a Method for Inorganic Lead

The available literature[3,4] indicated that at some sources likely to be tested a 2-hr sample taken at the normal isokinetic rate of 22 L min^{-1} could easily contain 500 mg quantities of the following difficult-to-solubilize Pb compounds: PbO, PbO_2, Pb_3O_4, $PbSO_4$, PbS, and $PbCl_2$. Thus, various solubilization methods were evaluated for their effectiveness in dissolving 500 mg and larger quantities of these compounds as well as elemental Pb.

This solubilization study showed that a procedure similar to one used in extracting Pb from ore[5] was the most effective. For example, it was determined that 10 ml of 50% (V/V) HNO_3/100 mg of Pb compound, 10 ml of 3% (V/V) H_2O_2 and 50 ml of hot (85° C) water would rapidly and completely solubilize all of the above Pb compounds in quantities up to 1.5 grams. In contrast 50% (V/V) HNO_3 alone would not dissolve large quantities of Pb_3O_4 or PbO_2.

After selecting the above HNO_3/H_2O_2 procedure as the tentative solubilization technique for inorganic Pb, additional laboratory experiments were done prior to collecting actual stack samples. These additional experiments showed that (1) two commercially available glass fiber filters, Reeve Angel 934AH and Gelman Spectrograde, yielded less than 0.2 μg Pb cm^{-2} when extracted with HNO_3/H_2O_2; (2) HNO_3 concentration in the sample did not interfere with the analysis by AA (no matrix effects) at least up to 10% acid concentration by volume; (3) tin, which has an intensive emission line 0.7 nm from the 283.3 nm Pb absorption line, did not interfere with the analysis for Pb when present in concentrations ten times higher than the Pb concentration; and (4) passing 7 m^3 of 2500 ppm SO_2 in air at a rate of 22 L min^{-1} through a 0.1 N HNO_3 solution that contained 60 mg Pb L^{-1} did not cause $PbSO_4$ to precipitate.

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Table I. Stack sampling results.

Plant	Sampling point	Run no.	Sampling time (Min)	Approx. rate L min^{-1}	Individual results in mg Pb m^{-3} M-13	M-13	M-13	M-5	M-17
Gray iron foundry	Baghouse outlet	1	60	22	93.2	93.5			
Lead storage battery	Baghouse outlet	1	60	22	16.4	15.0			
	Baghouse inlet	1	60	22	122.5	115.5			
		2	60	22	46.9	76.8			
		3	60	22	56.7	50.5			
		4	60	22	91.8	154.7			
Lead recovery furnace	Wet scrubber outlet	1	60	12	5.80	5.69			
		2	60	12	6.40	8.29[a]			
Secondary lead smelter	Wet scrubber outlet	1	180	22			1.50	1.60	1.57
		2	180	22			1.21	1.36	1.13
		3	180	22			1.44	1.30	1.73[b]
		4	180	22	0.59	0.59	0.64		
		5	180	22	1.11	1.09	1.26		
		6	180	22	1.23	1.15	1.23		

[a] One abnormally large particle was observed on the filter during sample recovery.
[b] Approximately 50% of the lead collected was in the impingers.

Since a general test method for inorganic Pb was desired, it was decided to evaluate the effectiveness of the EPA Method 13 train[6] for collecting Pb. In this train the sampled stack gas is passed through a glass-lined probe, then through three large impingers before contacting the filter. An advantage of this train over the EPA Method 5 train[7] (out-of-stack heated filter placed immediately behind the probe) is that filter heating is not required.

The Method 13 train was evaluated by taking samples from the stacks of a secondary lead smelter, a gray iron foundry, a lead storage battery plant and a lead recovery furnace at an alkyl lead manufacturing plant. In all tests a minimum of two trains was used in each sampling run with both trains simultaneously sampling at essentially the same point in the stack. In some of these tests a comparison of the Method 13 train was made vs. the EPA Method 5 train[7] and the EPA Method 17 train[8] (in-stack filter). In these comparative tests each Method 17 and Method 5 filter was followed by a complete Method 13 train to collect any Pb which passed through the filters.

Negotiations to collect stack samples from a primary copper and a primary lead smelter were not successful. However, dust samples were collected from three particulate control devices at a primary lead smelter (acid plant Cottrell dust, blast furnace dust, and cross ventilation dust) and two particulate control devices at a primary copper smelter (pug mill dust and converter flue dust).

All source samples were digested in 50% (V/V) HNO_3/3%H_2O_2/50 ml H_2O and analyzed for Pb. The efficiency of extraction of Pb from these samples was checked (1) by performing a second extraction on some of the filters and impinger residues using aqua regia; (2) by extracting 500 and 1000 mg portions of the smelter dust samples using acid volumes of 3, 4, 5, 6, 7, and 10 ml/100 mg of samples; and (3) by also extracting the smelter dust samples with $HNO_3/HClO_4$. At least one sample from each source was subjected to a Method of Standard Additions[9] to determine if matrix effects interfered in the analysis.

The results of these field studies are summarized in Tables I and II. From Table I it is apparent that the three types of sampling trains yielded equivalent results at the secondary lead smelter. For example, only one of the Method 13 trains that followed the Method 5 and Method 17 trains contained a measurable amount of Pb. In this one case—run 3, Method 17—it is possible that the in-stack filter was not properly seated on its support and leakage occurred around the filter. Other results from the analysis of the field samples are (1) no interfering elements or matrix effects were observed when the samples were analyzed by AA using the 283.3 nm and 217.0 nm absorption line; (2) no additional Pb was measured when an aqua regia extraction was done on residues from a HNO_3/H_2O_2 extraction of samples from the secondary lead smelter and lead recovery furnace; (3) the $HNO_3/HClO_4$ extraction of the primary copper and lead dust samples yielded results equivalent to those received from the HNO_3/H_2O_2 extraction of these samples (Table II); (4) approximately 50 to 60% of the Pb collected in the Method 13 trains at the secondary lead smelter, the lead recovery furnace, and the gray iron foundry was found on the filter; (5) the samples were stable for at least 1 month when stored in polyethylene or glass bottles; and (6) the impinger solutions could be taken to dryness on a hot plate without loss of sample.

Recommended Sampling and Analysis Procedure for Inorganic Lead

A standard EPA Method 5 particulate sampling train containing 100 ml of 0.1 N HNO_3 in each of the first two impingers is recommended for sampling for Pb. Although most of the testing conducted during this study employed the EPA Method 13 sampling train configuration, the Method 5 train is recommended over the Method 13 train for the following reasons:

1. At three of the four sources tested, approximately 50% of the total Pb collected was found on the Method 13 train's filter, an indication that the impingers did not quantitatively collect the Pb sampled.

Table II. Analysis of dust samples from primary smelters.

Plant	Sample type	% Pb in dust sample by weight HNO_3/H_2O_2[a]	$HNO_3/HClO_4$[b]
Primary copper smelter	Converter flue dust	1.5, 1.5, 1.5	1.4, 1.6
	Pug mill dust	6.4, 6.7, 6.5	6.8, 6.7, 6.5
Primary lead smelter	Acid plant Cotrell dust	57.3, 56.8	57.7, 60.2, 59.2
	Blast furnace dust	52.7, 53.0, 52.7	55.9, 53.5, 53.8
	Dross ventilation baghouse dust	33.2, 33.1	33.0, 32.3, 32.5

[a] Analysis done by this laboratory.
[b] Analysis done by ASARCO, Salt Lake City, UT.

2. Most of the facilities covered under the Air Quality Standard for Pb now measure their particulate emissions using a Method 5 sampling train. It is also likely that their Pb emissions will be in the form of a particulate that can be quantitatively collected on the high efficiency, low-lead glass fiber filters now available. Thus, a plant could conduct testing for Pb and for particulate simultaneously.
3. The use of the Method 5 train will permit a simpler sample recovery procedure to be used compared to that required if the Method 13 train were used.

The primary reason for recommending the Method 5 train configuration rather than the Method 17 train configuration is the tendency for the in-stack filter to slip out of position, thereby allowing particulate Pb to bypass the filter. This event likely occurred in sampling run 3 at the secondary lead smelter and has also been observed in other applications of Method 17.[10]

It is recommended that the samples be digested using a minimum of 10 ml 50% (V/V) HNO_3/100 mg of sample, 10 ml of 3% H_2O_2, and 50 ml of hot water and be analyzed using flame atomic absorption spectrometry.

Development of a Method for Alkyl Lead

Review of the available literature and correspondence with chemists from two alkyl lead manufacturing plants[11,12] indicated that dilute ICl solution would effectively collect alkyl lead compounds. For example, Moss and Browett[13] had achieved collection efficiencies between 98 and 100% for tetraethyl lead (TEL) and tetramethyl lead (TML) in a single Dreshel bubbler when sampling at room temperature at a flow rate of 2 L min^{-1}. Lead concentrations sampled by Moss and Browett ranged from 0.8 to 3.5 mg lead alkyl/m^3, and sample volumes ranged from 600 to 800 L. Snyder[11] showed that the collection efficiency of a single Smith-Greenburg impinger containing 150 mL of 0.1 M ICl was 92 to 94% for TML in the concentration range 1.0 μg to 6.0 g Pb m^{-3}. Similar data were not available for TEL, but at 400 μg Pb m^{-3} the collection efficiency of the above impinger was 95 to 98%.[11] However, experimental data concerning collection efficiency as a function of flow rate, ICl concentration, and collecting solution temperature were not available and the above studies[11,13] were done using synthetic atmospheres rather than actual process streams.

Prior to conducting field studies, the sample storage and analysis portions of the tentative test method were evaluated using motor-mix solutions obtained from Ethyl Corp., Detroit, MI. Motor-mix, which is a mixture of alkyl lead compound(s), ethylene dichloride, ethylene dibromide, and a dye formulated to contain 39.39 ± 0.10% Pb by weight, is the medium used to store alkyl lead compounds prior to use. Three motor-mix blends were used in the study; one contained only TEL, another contained only TML, and the third contained equal amounts of TML and TEL.

The above motor-mixes were first dissolved in anhydrous methanol in the ratio of 1:50, then diluted further using 0.1 M, 0.2 M, and 0.3 M ICl. Final dilutions ranged from 0.5 to 25 μg Pb mL^{-1}. The samples were found to be stable for at least 2 months when stored in the dark at room temperature in either glass or polyethylene containers. Other experiments established that (1) the AA calibration curves for TML and TEL in 0.1 M and 0.2 M ICl are identical to those for corresponding Pb concentrations in dilute HNO_3 (1–10% nitric) when a lean, blue oxidizing flame is used; (2) 0.1 M, 0.2 M, and 0.3 M ICl solutions do not absorb at either 217.0 or 283.3 nm (the two principal Pb lines used in AA spectrometry); and (3) alkyl lead in ICl solutions can be taken to dryness on a hot plate, heated until all color has disappeared, dissolved in HNO_3, then analyzed for Pb by flame AA without loss of Pb.

Samples were then taken from a process vent stack at an alkyl lead manufacturing plant. This stack gas contained approximately 500 mg TEL m^{-3} and several percent hydrocarbons with air as the diluent. Five sampling runs were achieved with four sampling trains sampling simultaneously from the same manifold in each run. Each sampling train contained two Smith-Greenburg impingers connected in series with a glass connection and was backed up with a tube containing 4 to 6 g of activated charcoal. Each impinger contained 125 mL of either 0.1 M or 0.2 M ICl.

In each sampling run the effect of ICl concentration (0.1 M vs. 0.2 M), flow rate (1.5 vs. 2.8 L min^{-1}), and collection temperature (0°C vs. the ambient temperature of 10°C) was evaluated using the ruggedness testing procedure of Youden.[14] Each sampling run represented a complete ruggedness test in itself (Table III). The effect of these sampling conditions on collection efficiency was evaluated in each of the 5 sampling runs. At the same time, the capacity of the sampling train for TEL was evaluated by using a different sampling time for each run, that is 20, 40, 60, 90, and 120 min.

Table III. Ruggedness test design used in sampling for tetraethyl lead.

Variable	Sampling train			
	1	2	3	4
ICl conc.	0.2 M	0.1 M	0.2 M	0.1 M
Flow rate	low	high	high	low
ICl temp.	0°C	0°C	10°C	10°C

All samples were taken on the same day, packed in ice, returned to the laboratory, and analyzed within 48 hr from the time they were collected. The amount of Pb collected in each impinger was determined by diluting the sample with the appropriate ICl solution (0.1 M, 0.2 M), followed by analysis using flame AA spectrometry against both TEL in ICl and inorganic lead in dilute HNO_3 standards. To check for breakthrough, the charcoal samples from the 120 min duration sampling run were digested in hot aqua regia, filtered, the extract taken to dryness, digested in concentrated HNO_3 and taken to dryness, then taken up in 100 ml of 5% HNO_3 for analysis by flame AA. Lead was not found in any of the four charcoal samples studied, so other charcoal samples were not analyzed.

The results from the 20 min and 120 min runs are presented in Table IV. The results from the other three runs were similar. From the analysis of all samples, it is concluded that (1) the collection efficiency (for TEL) of a single Smith-Greenburg impinger that contains 125 ml of 0.1 M or 0.2 M ICl is better than 98% percent when sampling Pb concentrations from 375 to 575 mg TEL m^{-3} at flow rates between 1.1 and 2.8 L min^{-1}; (2) decreasing the impinger bath temperature and the flow rate and increasing the ICl concentration did not

Table IV. Distribution of lead in the alkyl lead sampling train.

Time (min)	Train no.	mg Pb in first impinger	mg Pb in second impinger	Sampling rate (L min^{-1})
20	1	7.11	0.06	1.33
	2	10.22	0.15	2.00
	3	12.65	0.21	2.60
	4	6.20	0.03	1.12
120	1	49.73	0.23	1.42
	2	74.52	0.52	1.93
	3	96.10	2.65	2.45
	4	52.46	0.61	1.48

significantly improve the overall collection efficiency of the first impinger compared to the second impinger under the experimental conditions studied; (3) the collected samples, which contained 0.005 to 150 mg Pb mL^{-1}, were found to be stable for at least 1 month when stored in the dark at ambient temperature in either glass or polyethylene bottles; (4) the samples could be taken to dryness on a hot plate, heated until all color disappeared, dissolved in dilute HNO_3, then analyzed for Pb without loss of Pb; and (5) use of the Method of Standard Additions[9] confirmed that an accurate analysis can be obtained when the AA spectrophotometer is calibrated with standard solutions of inorganic Pb in dilute HNO_3.

Recommended Sampling and Analysis Procedure for Alkyl Lead

Two Smith-Greenburg impingers, each containing 125 mL of 0.2 M ICl and connected in series using all glass fittings, are recommended for collecting alkyl lead compounds from stack gases. Two impingers rather than a single impinger are recommended, because experiments conducted in this study (Table IV) and work done by others[11,13] indicate that the collection efficiency of a single impinger for alkyl lead is less than 100%. Use of 0.2 M ICl rather than 0.1 M ICl is recommended primarily because of the larger capacity of 0.2 M ICl for alkyl lead compounds.

It is also recommended that the impinger temperature be maintained between 0° and 10°C and that the sampling rate be maintained between 1.5 and 3 L min^{-1}. Temperature and flow rates outside these limits may be acceptable if experimental data are obtained to confirm that the collection efficiency is essentially 100% at these other temperatures and flow rates.

The samples can be analyzed directly by flame atomic absorption (AA) spectrometry using a lean, blue flame, but, it is recommended that the accuracy of the analysis be confirmed on at least one sample as follows: take an aliquot of the sample to dryness on a hot plate, heat until all color has disappeared, digest in 10 ml of 50% (V/V) HNO_3, dilute to volume with distilled, deionized water, and analyze for Pb using flame AA spectrometry and the Method of Standard Additions.[9]

Simplified Method for Determining Alkyl Lead Content of Ambient Air

The total Pb emissions to the atmosphere from the six alkyl lead manufacturing plants in the U.S. are estimated to be 1100 ton/year[3] and it seems likely that some ambient air monitoring will be required at these plants. The two methods presently used to measure ambient alkyl lead compounds employ simple collection techniques, that is, ICl[15] or charcoal,[16] but have tedious, time-consuming extraction procedures. It seems likely that the sampling procedure of Purdue,[15] and the analytical procedure described here can be combined to give a less tedious method. For example, if the total alkyl lead concentration in the sample exceeded 0.5 μg Pb mL^{-1}, the samples could be analyzed by direct aspiration into the flame. If the sample concentration was less than 0.5 μg Pb mL^{-1}, then the samples could be concentrated by taking them to dryness and solubilizing the residue with HNO_3.

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